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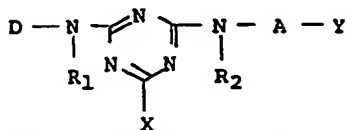
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(64) Reactive-dye-containing aqueous liquid composition.

(67) An aqueous liquid dye composition comprising 5 to 50% by weight of a reactive dye represented by the following formula,



wherein D denotes a sulfo group-containing organic dye residue, R<sub>1</sub> and R<sub>2</sub> independently of one another denote a hydrogen atom or a C<sub>1</sub> to C<sub>4</sub> alkyl group unsubstituted or substituted with a halogen atom or a hydroxyl, cyano, C<sub>1</sub> to C<sub>4</sub> alkoxy, carboxy, carbamoyl, C<sub>1</sub> to C<sub>4</sub> alkoxycarbonyl, C<sub>1</sub> to C<sub>4</sub> alkylcarbonyloxy, sulfo or sulfamoyl group, A denotes a phenylene group unsubstituted or substituted with one or two members selected from methyl, ethyl, methoxy, ethoxy, chlorine, bromine and sulfo, or a naphthylene group unsubstituted or substituted with one sulfo group, X denotes a halogen atom, and Y is a group of -SO<sub>2</sub>CH=CH<sub>2</sub> or -SO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Z in which Z is a splittable group by the action of an alkali, 0.1 to 10% by weight of ε-caprolactam and the balance of water, the composition having a pH value of 3 to 7, which can be stored for a long period of time at a low temperature such as 5°C or lower without deterioration in its solution state.

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REACTIVE DYE-CONTAINING  
AQUEOUS LIQUID COMPOSITION

1           The present invention relates to a reactive  
dye-containing aqueous liquid composition excellent in  
storage stability at a low temperature and a method for  
dyeing or printing fiber materials using the composi-  
5   tion.

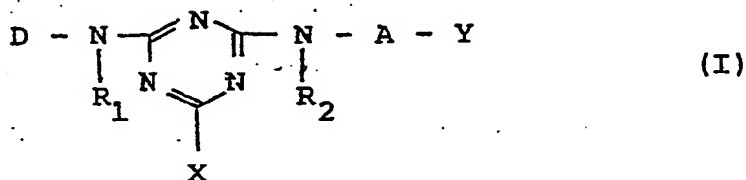
Industrial dyeing or printing of fiber  
materials with reactive dyes has been carried out usual-  
ly in an aqueous medium, and when used for the dyeing or  
printing, the reactive dyes commercially available in  
10 the form of powder or granule must be dissolved in the  
aqueous medium using hot water.

In recent years, dyeing or printing systems in  
a dye house have been actively mechanized and automated  
in many aspects, and therefore the reactive dyes have  
15 been eagerly required to be made into a form suitable  
for an automatic weighing and dispensing system.

An aqueous liquid composition of the reactive  
dye is now considered to be very favorable, because it  
is suitable for the automatic weighing and dispensing  
20 system and causes no powder-scattering on the handling,  
resulting in no pollution of a working environment, and  
moreover it can serve saving energy and labor. Thus, it  
has been required to make a reactive dye-containing  
aqueous liquid composition having no problem from  
25 industrial point of view.

1 In general, however, although the reactive  
dye-containing aqueous liquid composition is relatively  
stable at ordinary temperatures, it is natural that in  
the winter the aqueous liquid composition is allowed to  
5 stand at a temperature of 5°C or lower through manu-  
facturing, custody, transportation, shipment, storage or  
the like, so that the reactive dye contained therein  
lowers its solubility and then precipitates.

A reactive dye of the following formula (I),



10 wherein D denotes a sulfo group-containing organic dye  
residue, R<sub>1</sub> and R<sub>2</sub> independently of one another denote a  
hydrogen atom or a C<sub>1</sub> to C<sub>4</sub> alkyl group unsubstituted or  
substituted with a halogen atom or a hydroxyl, cyano, C<sub>1</sub>  
to C<sub>4</sub> alkoxy, carboxy, carbamoyl, C<sub>1</sub> to C<sub>4</sub> alkoxy-  
15 carbonyl, C<sub>1</sub> to C<sub>4</sub> alkylcarbonyloxy, sulfo or sulfamoyl  
group, A denotes a phenylene group unsubstituted or sub-  
stituted with one or two members selected from methyl,  
ethyl, methoxy, ethoxy, chlorine, bromine and sulfo, or  
a naphthylene group unsubstituted or substituted with  
20 one sulfo group, X denotes a halogen atom, and Y is a group of the  
formula -SO<sub>2</sub>CH=CH<sub>2</sub> or -SO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Z in which Z is a  
group which can be removed by the action of alkali, has been

1 extensively used for dyeing or printing fiber materials  
because of its characteristic dye performances, but it  
is easy to precipitate at a low temperature such as 5°C  
or lower, because of its relatively low solubility in  
5 water. If the reactive dyes of the formula (I) are  
formed into an aqueous liquid composition in a conven-  
tional manner, the liquid composition is easy to  
precipitate the reactive dye at a low temperature. If  
the precipitate-containing liquid composition is used as  
10 it is for the dyeing or printing, there are caused  
problems due to inaccuracy of the weighing as well as  
troubles such as pipe-stopping of automatic weighing and  
dispensing devices. While, in order to dissolve the  
precipitate, it is necessary to heat the liquid  
15 composition to a temperature of about 80°C. In this  
case, however, there are many problems to be solved with  
respect to the operation and stability of the reactive  
dye per se at such a high temperature.

The present inventors have undertaken exten-  
20 sive studies to improve the aqueous liquid composition  
containing such reactive dyes having problems in the  
dissolution stability at a low temperature, and as a  
result found that incorporation of  $\epsilon$ -caprolactam can  
solve such problems.

25 The present invention provides an aqueous  
liquid dye composition comprising 5 to 50% by weight of  
a reactive dye of the above formula (I), 0.1 to 10% by  
weight of  $\epsilon$ -caprolactam and the balance of water, the

1 composition having a pH value of 3 to 7.

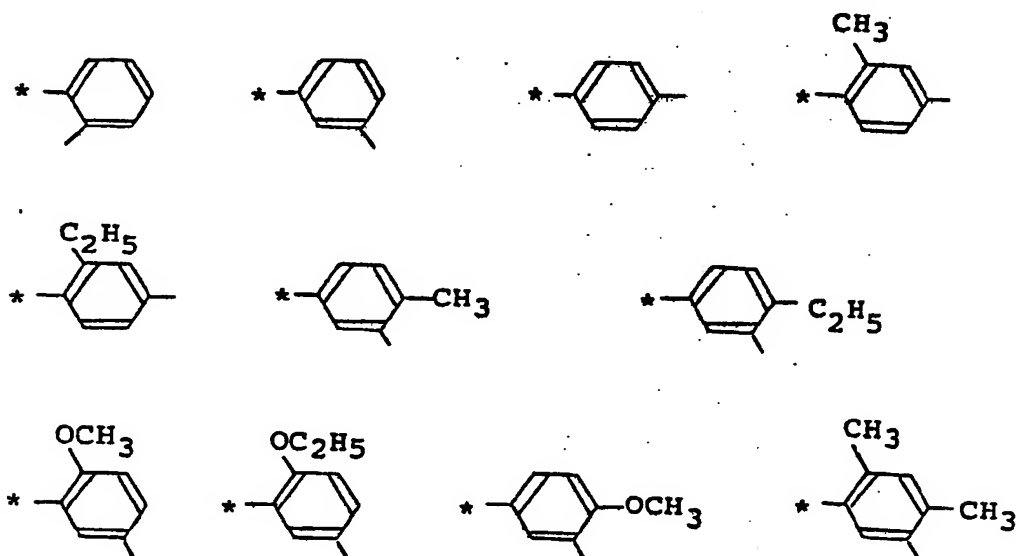
With respect to the reactive dyes of the formula (I) usable in the present invention, the residue D of sulfo group-containing organic dyes includes, for  
5 example, residues of monoazo dyes, polyazo dyes such as bisazo dyes, metal complex monoazo and bisazo dyes, metal formazan dyes, anthraquinone dyes, metal phthalocyanine dyes, stilbene dyes, oxazine dyes, dioxazine  
10 dyes, triphenylmethane dyes, phenazine dyes, xanthene quinone dyes, naphthoquinone dyes, pyrene-quinone dyes, perilenetetracarboimide dyes, nitro- or azomethine dyes and the like. The metal in the metal complex azo, metal formazan and metal phthalocyanine  
dyes includes Cu, Cr, Co, Ni, Fe and the like.

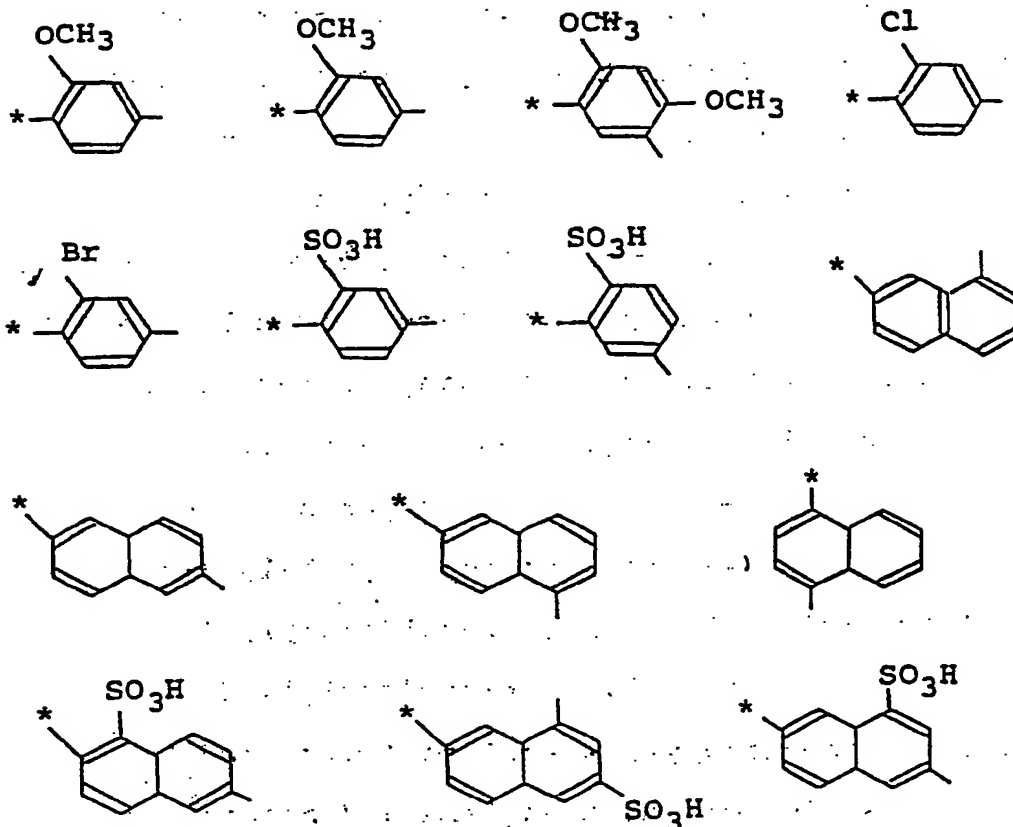
15 The alkyl group represented by R<sub>1</sub> and R<sub>2</sub> may be unsubstituted or substituted with a member preferably selected from hydroxy, cyano, alkoxy, halogeno, carboxy, carbamoyl, alkoxycarbonyl, C<sub>1</sub> to C<sub>4</sub> alkylcarbonyloxy, sulfo, sulfamoyl and the like.

20 Preferable examples of R<sub>1</sub> and R<sub>2</sub> are hydrogen, methyl, ethyl, n-propyl, iso-propyl n-butyl, iso-butyl, sec-butyl, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 2-hydroxybutyl, 3-hydroxybutyl, 2-hydroxybutyl, 3-hydroxy-  
25 butyl, 4-hydroxybutyl, 2,3-dihydroxypropyl, 3,4-dihydroxybutyl, cyanomethyl, 2-cyanoethyl, 3-cyanopropyl, methoxymethyl, ethoxymethyl, 2-methoxyethyl, 2-ethoxyethyl, 3-methoxypropyl, 3-ethoxypropyl, 2-hydroxy-3-methoxypropyl, chloromethyl, bromomethyl, 2-chloroethyl, 2-bromoethyl,

- 1 3-chloropropyl, 3-bromopropyl, 4-chlorobutyl, 4-bromo-  
butyl, carboxymethyl, 2-carboxyethyl, 3-carboxypropyl,  
4-carboxybutyl, 1,2-dicarboxyethyl, carbamoylmethyl, 2-  
carbamoylethyl, 3-carbamoylpropyl, 4-carbamoylbutyl,  
5 methoxycarbonylmethyl, ethoxycarbonylmethyl, 2-methoxy-  
carbonylethyl, 2-ethoxycarbonylethyl, 3-methoxycarbonyl-  
propyl, 3-ethoxycarbonylpropyl, 4-methoxycarbonylbutyl,  
4-ethoxycarbonylbutyl, methylcarbonyloxymethyl, ethyl-  
carbonyloxymethyl, 2-methylcarbonyloxyethyl, 2-ethyl-  
10 carbonyloxyethyl, 3-methylcarbonyloxypropyl, 3-ethyl-  
carbonyloxypropyl, 4-methylcarbonyloxybutyl, 4-ethyl-  
carbonyloxybutyl, sulfomethyl, 2-sulfoethyl, 3-  
sulfopropyl, 4-sulfobutyl, sulfamoylmethyl, 2-sulfamoyl-  
ethyl, 3-sulfamoylpropyl, 4-sulfamoylbutyl and the like.

- 15 Examples of the phenylene and naphthylene  
groups represented by A area as follows:





1 (In the above formulae, the asterisked linkage is intended to mean the linkage to the group,  $-\text{NR}_1-$ .)

The halogen represented by X includes chlorine and fluorine.

5 The splittable group represented by Z includes a sulfuric acid ester group, thiosulfuric acid ester group, phosphoric acid ester group, acetic acid ester group and halogen atoms.

10 The reactive dye of the formula (I) can be produced, for example, by subjecting any one of an amine compound represented by the following formula (II),



1 wherein D and R<sub>1</sub> are as defined above, or an aromatic amine compound represented by the following formula (IV),



wherein R<sub>2</sub>, A and Y are as defined above, to condensation with a trihalogenotriazine represented by the following formula (III),



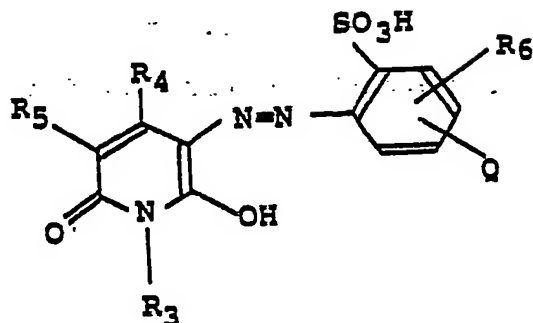
wherein X is as defined above, followed by condensation with the remaining one of (IV) or (II).

Among the reactive dyes of the formula (I),  
10 particularly preferred ones are exemplified as follows:

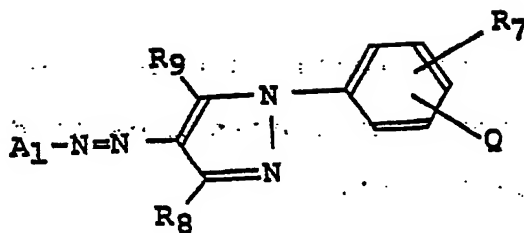


1. Monoazo dyes

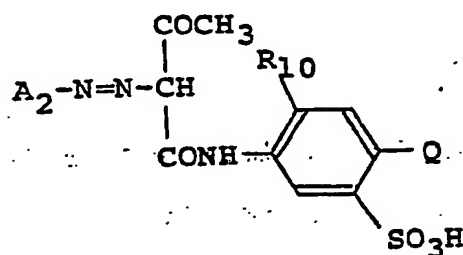
Ia. Pyridone dyes



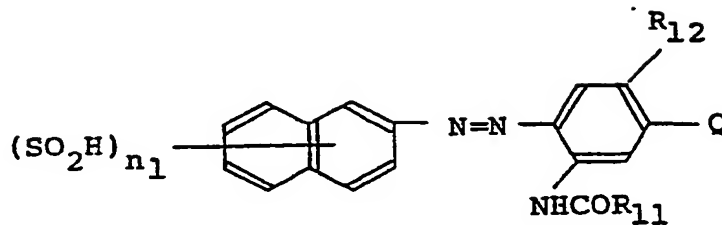
Ib. Pyrazolone dyes



Ic. Acetoacetic acid anilide dyes



5 Id. Naphthalene dyes

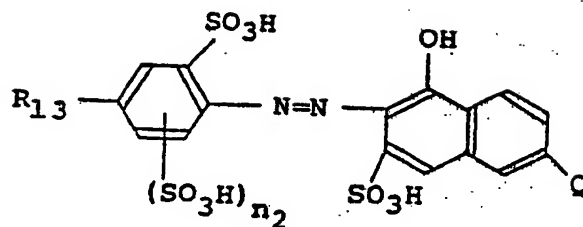


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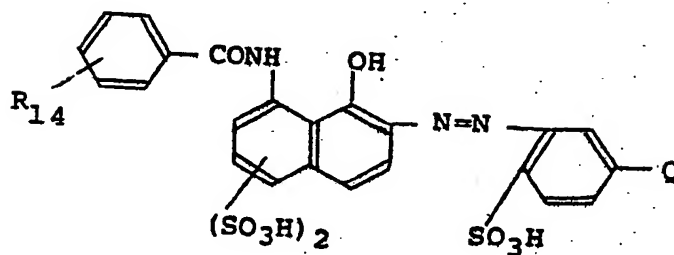
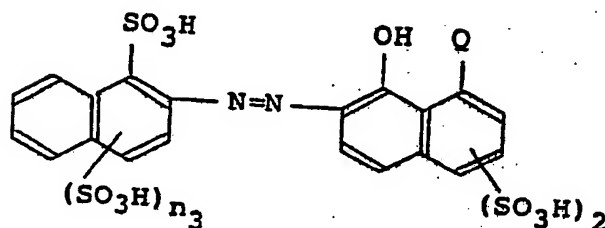
Ie. J acid dyes

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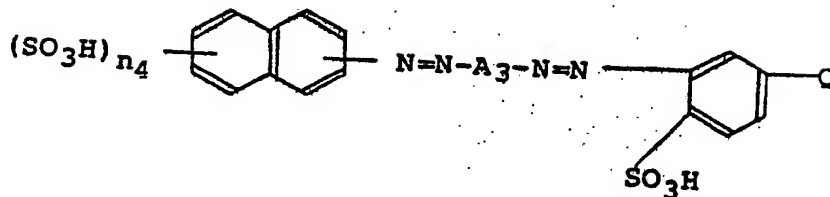


If. H acid or K acid dyes



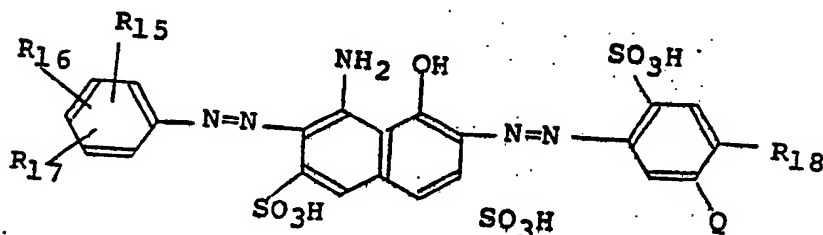
2. Bisazo dyes

Ig



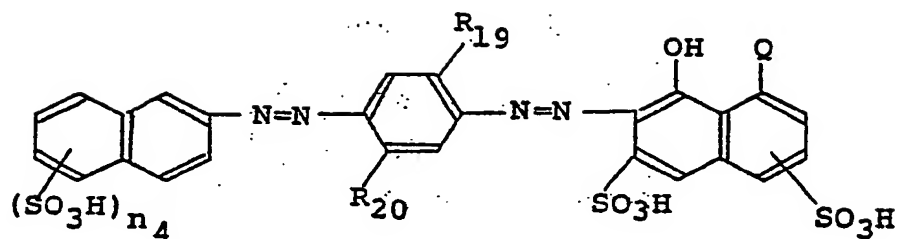
5

Ih



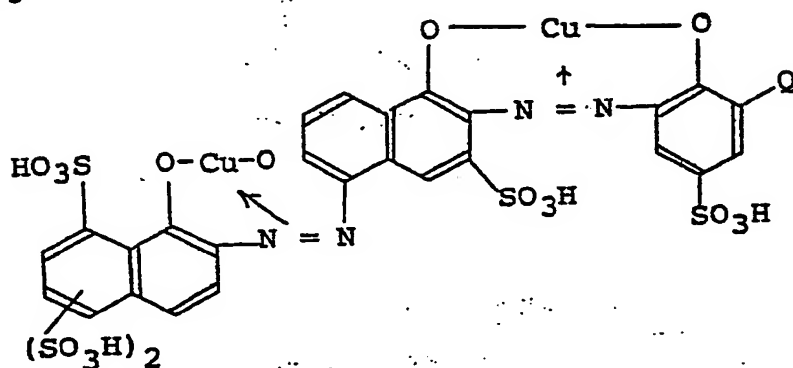
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Ii

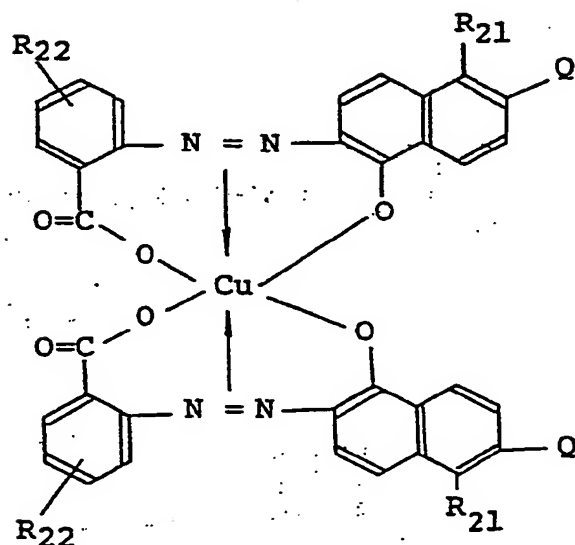


### 3. Metal bisazo-dyes

Ij

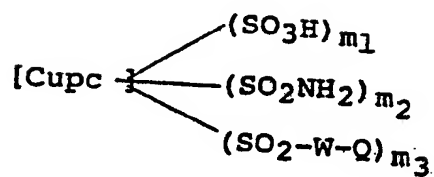


Ik



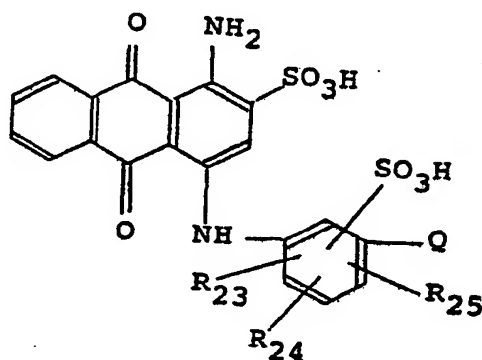
1 4. Phthalocyanine dyes

Il



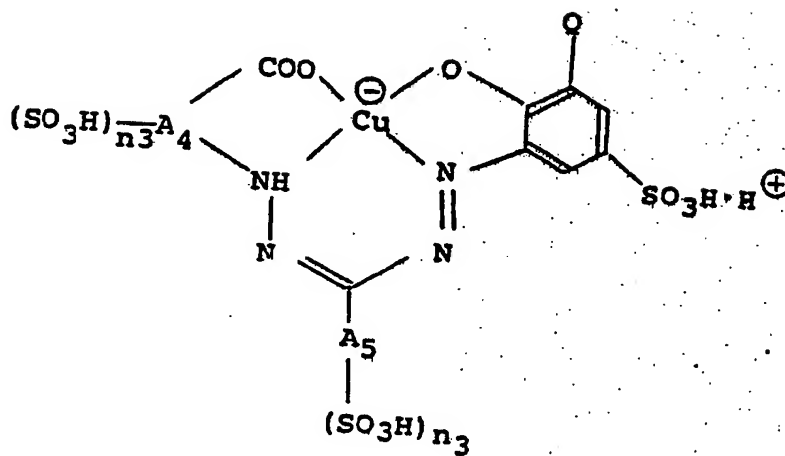
5. Anthraquinone dyes

Im

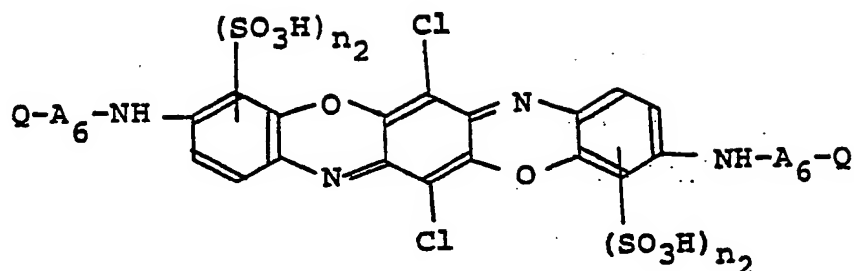


5 6. Formazan dyes

In



1 7. Dioxazine dyes



In the above formulas, definitions of all symbols are as follows:

- R<sub>3</sub>: hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl,
- 5 R<sub>4</sub>: C<sub>1</sub>-C<sub>4</sub> alkyl,
- R<sub>5</sub>: hydrogen, cyano, -CONH<sub>2</sub> or sulfo-C<sub>1</sub>-C<sub>4</sub> alkyl,
- R<sub>6</sub>: hydrogen or sulfo,
- R<sub>7</sub>: hydrogen, sulfo or C<sub>1</sub>-C<sub>4</sub> alkyl,
- 10 R<sub>8</sub>: methyl, carboxy or methoxycarbonyl,
- R<sub>9</sub>: hydroxy or amino,
- R<sub>10</sub>: methoxy, ethoxy or sulfo,
- R<sub>11</sub>: methyl, amino or phenyl,
- R<sub>12</sub>: C<sub>1</sub>-C<sub>4</sub> alkyl,
- 15 R<sub>13</sub>: C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> alkoxy,
- R<sub>14</sub>: hydrogen, nitro, sulfo, chloro, carboxy, C<sub>1</sub>-C<sub>4</sub> alkyl or the like,
- R<sub>15</sub>, R<sub>16</sub>, R<sub>17</sub>: hydrogen, chloro, methyl, methoxy, sulfo or carboxy,
- 20 R<sub>18</sub>: hydrogen or methyl,
- R<sub>19</sub>, R<sub>20</sub>: hydrogen, C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> alkoxy,

- 1 R21: hydrogen or sulfo,  
R22: hydrogen, C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> alkoxy, sulfo  
or acetylamino,  
R23, R24, R25: C<sub>1</sub>-C<sub>4</sub> alkyl,
- 5 A1: unsubstituted or substituted phenylene  
(examples of the substituent being 1 to 3  
members selected from methyl, ethyl, methoxy,  
ethoxy, halogen, acetylamino, propionylamino,  
nitro, sulfo and carboxy) or naphthalene un-  
10 substituted or substituted with 1 to 3  
sulfoes,
- A2: sulfophenyl substituted with methyl, ethyl,  
methoxy, ethoxy, phenoxy, acetylamino,  
propionylamino, HOOCCH<sub>2</sub>CH<sub>2</sub>CONH- or  
15 HOOCCH=CHCONH-, or naphthylene substituted  
with two or three sulfoes,
- A3: residue of naphthalenesulfonic acids such as H  
acid and K acid,
- A4: unsubstituted or substituted phenylene  
20 (examples of the substituents being halogen,  
nitro, C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> alkoxy, sulfamoyl,  
N- or N,N-di-C<sub>1</sub>-C<sub>4</sub> alkylsulfamoyl, C<sub>1</sub>-C<sub>4</sub>  
alkylsulfonyl or phenylsulfonyl),
- A5: unsubstituted or substituted phenylene  
25 (examples of the substituents being methyl,  
ethyl, methoxy, ethoxy, halogen or sulfamoyl),
- A6: phenylene or naphthylene unsubstituted or  
substituted 1 to 3 sulfoes,

- 1 W: aminoalkyl residue such as  $-N \begin{cases} \text{H or CH}_3 \\ (\text{C}_2\text{H}_4)_{1-3} \end{cases}$
- $m_1$ : 1 or 2,
- $m_2$ : 0, 1 or 2,
- $m_3$ : 1 or 2, provided that  $m_1 + m_2 + m_3 \leq 4$ ,
- 5  $n_1$ : 2 or 3,
- $n_2$ : 0 or 1,
- $n_3$ : 1 or 2,
- $n_4$ : 1, 2 or 3,
- Q:  $-\text{SO}_2\text{CH}_2\text{CH}_2\text{Z}$  (Z being as defined above),
- 10 preferably  $-\text{SO}_2\text{CH}_2\text{CH}_2\text{OSO}_3\text{H}$ .

In the production of the aqueous liquid composition in accordance with the present invention, the reactive dye-containing reaction mixture obtainable, for example, through the production method described above,

15 may be used as it is. When the reaction mixture contains too large amount of water, the dye content can be controlled in a manner such that the reaction mixture may be concentrated, for example, by evaporation of a part of water in vacuo, or the reactive dye powder obtainable by

20 drying a part of the reaction mixture may be mixed with the remaining reaction mixture. Alternatively, a wet cake obtainable through conventional manners such as salting out of the reaction mixture and filtration, or a powder obtainably by drying the wet cake, may be used for the

25 production of the present aqueous liquid composition by dissolving it in a pre-determined amount of water.

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1           The content of the reactive dye can be deter-  
mined within a range of 5 to 50% by weight based on the  
weight of the aqueous liquid composition depending on  
the solubility of the reactive dye to be used, amounts  
5 of  $\epsilon$ -caprolactum, inorganic salts usually inevitably  
contained therein, and other additives, if any, and  
other factors such as needs of the industrial world.

$\epsilon$ -Caprolactam is used in an amount of from 0.1  
to 10% by weight, preferably from 0.5 to 8% by weight,  
10 based on the weight of the aqueous liquid composition.

The aqueous liquid composition of the present  
invention may contain other additives such as pH  
buffers, surfactants, dyeing auxiliary agents, hydro-  
tropic agents, defoaming agents, antifreezing agents,  
15 antiseptics and the like. The pH buffers are those  
inert to the reactive dye, and include, for example,  
sodium or potassium acetate, sodium or potassium  
oxalate, sodium borate, sodium or potassium phosphates,  
and a mixture thereof.

20           The aqueous liquid composition can be pre-  
pared, for example, in the following manner.

An aqueous solution of the reactive dye is  
mixed with the pre-determined amount of the additives  
including  $\epsilon$ -caprolactam to form a clear solution, and  
25 the clear solution is adjusted to a pH within a range of  
3 to 7 using an acid such as sulfuric acid, hydrochloric  
acid, acetic acid and the like, or an alkali such as  
sodium hydroxide, sodium carbonate and the like.



1    Thereafter, water is added to the clear solution to  
obtain the reactive dye-containing aqueous liquid  
composition having the desired dye content.

Notwithstanding a relatively high content of  
5    inorganic salts because of the reactive dye being used  
as it is without removal of the inorganic salts, the  
aqueous liquid composition prepared in accordance with  
the present invention can be stably stored for a long  
period of time at a low temperature of 5°C or below, for  
10    example, no precipitation of the reactive dye appears  
even after storage for 2 months at 0°C.

Moreover, a low viscosity (about 10 cps or  
lower) of the present aqueous liquid composition can be  
stably kept for a long period of time, and therefore the  
15    present composition can be applied to various kinds of  
automatic weighing and dispensing devices.

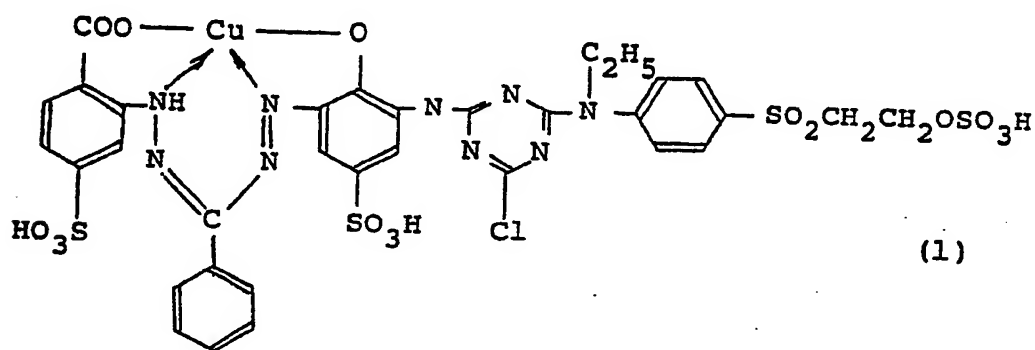
The present aqueous liquid composition can be  
used for dyeing or printing natural or synthetic fiber  
materials, particularly such as paper, cellulose fibers,  
20    polyamide fibers, wools and the like in a conventional  
manner, thereby giving dyed products which are equal to  
those obtainable using the reactive dye in the form of  
powder or granule.

The present invention is illustrated in more  
25    detail with reference to the following Examples, which  
are only illustrative and not intended to limit the  
scope of the present invention. In Examples, parts and  
% are by weight.

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1 Example 1

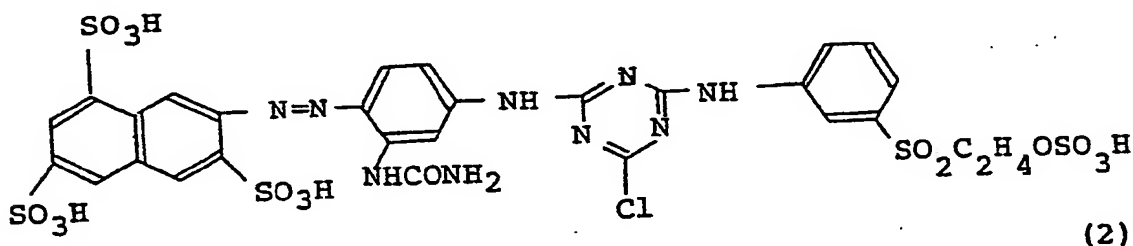
ε-Caprolactam (30 parts) was mixed with a reaction mixture (900 parts) which was a dye solution obtained by a known method having 12% in a content of a reactive dye represented by the formula (1) described below, 2% in a sodium chloride content and 1.5% in a sodium sulfate content. The mixture was formed into a clear solution, and sodium acetate (5 parts) was dissolved therein. The resulting solution was adjusted to pH 5.0 using 10% sulfuric acid, and then mixed with water to make the whole 1000 parts. A part of the aqueous liquid composition was stored for 2 months at 0°C. Then, the composition was found to have a stable solution state without precipitation of the reactive dye.



Example 2

ε-Caprolactam (30 parts) was mixed with a reaction mixture (900 parts) which was a dye solution obtained by a known method having 11% in a content of a reactive dye represented by the formula (2) described below, 4% in a sodium chloride content and 1% in a

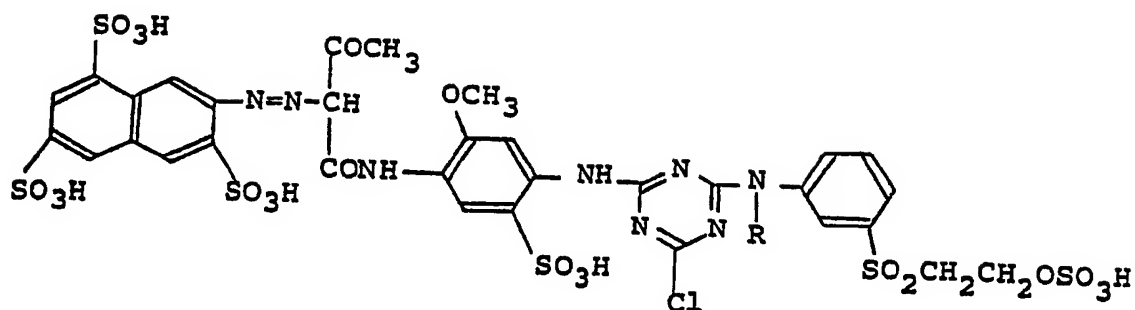
1 sodium sulfate content. The mixture was formed into a clear solution, and sodium acetate (5 parts) was dissolved therein. The resulting solution was adjusted to pH 5.3 using 10% sulfuric acid, and then mixed with  
 5 water to make the whole 1000 parts. A part of the aqueous liquid composition was stored for 2 months at 0°C. Then, the composition was found to have a stable solution state without precipitation of the reactive dye.



### 10 Example 3

$\epsilon$ -Caprolactam (50 parts) was mixed with a reaction mixture (900 parts) which was a dye solution obtained by a known method having 16% in a content of a reactive dye represented by the formula (3) described  
 15 below, 2% in a sodium chloride content and 1% in a sodium sulfate content. The mixture was formed into a clear solution, and sodium acetate (5 parts) was dissolved therein. The resulting solution was adjusted to pH 5.5 using 10% sulfuric acid, and then mixed with  
 20 water to make the whole 1000 parts. A part of the aqueous liquid composition was stored for 1 month at 0°C. Then, the composition was found to have a stable

- 1 solution state without precipitation of the reactive dye.



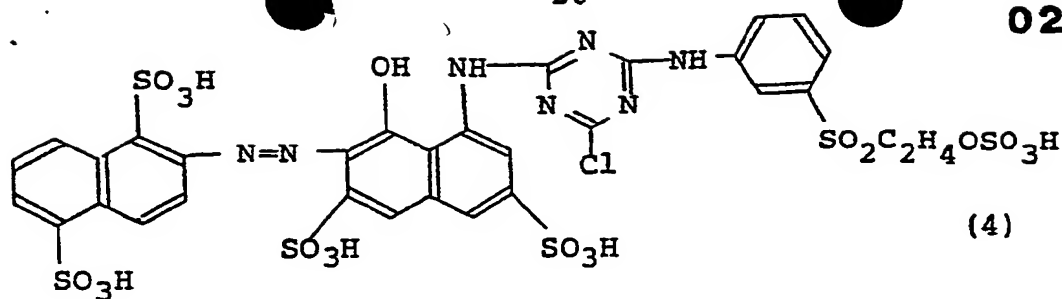
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Mixture of dyes having hydrogen and ethyl as R, respectively.

#### 5 Example 4

$\epsilon$ -Caprolactam (1 part) was mixed with a reaction mixture (900 parts) which was a dye solution obtained by a known method having 20% in a content of a reactive dye represented by the formula (4) described below, 4.5% in a sodium chloride content and 2% in a sodium sulfate content. The mixture was formed into a clear solution, and sodium acetate (10 parts) was dissolved therein. The resulting solution was adjusted to pH 5.3 using 10% sulfuric acid, and then mixed with water to make the whole 1000 parts. A part of the aqueous liquid composition was stored for 2 months at 0°C. Then, the composition was found to have a stable solution state without precipitation of the reactive dye.

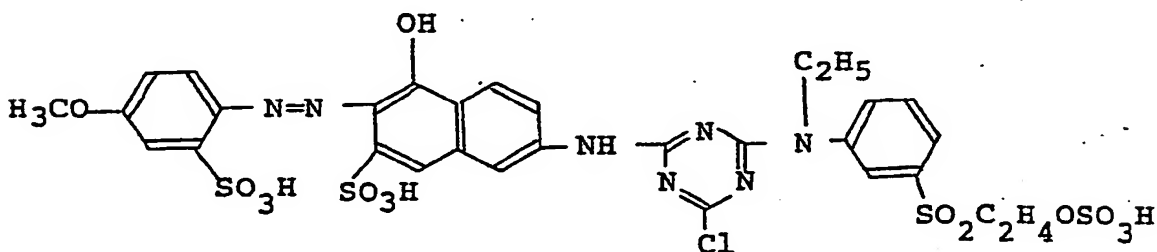
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# 1 Example 5

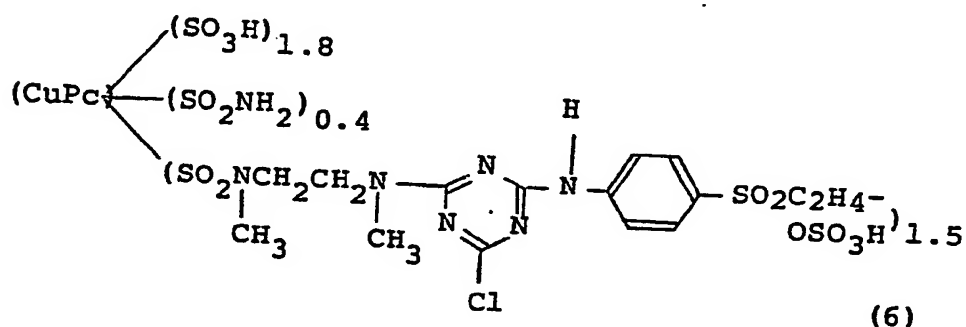
ε-Caprolactam (10 parts) was mixed with a reaction mixture (900 parts) which was a dye solution obtained by a known method having 10% in a content of a reactive dye represented by the formula (5) described below; 3% in a sodium chloride content and 1% in a sodium sulfate content. The mixture was formed into a clear solution, and sodium acetate (5 parts) was dissolved therein. The resulting solution was adjusted to pH 5.5 using 10% sulfuric acid, and then mixed with water to make the whole 1000 parts. A part of the aqueous liquid composition was stored for 1 month at 0°C. Then, the composition was found to have a stable solution state without precipitation of the reactive dye.



(5)

1 Example 6

5  $\epsilon$ -Caprolactam (30 parts) was mixed with a  
 reaction mixture (900 parts) which was a dye solution  
 obtained by a known method having 10% in a content of a  
 reactive dye represented by the formula (6) described  
 below, 5% in a sodium chloride content and 0.5% in a  
 sodium sulfate content. The mixture was formed into a  
 clear solution, and sodium acetate (5 parts) was dis-  
 solved therein. The resulting solution was adjusted to  
 10 pH 5.5 using 10% sulfuric acid, and then mixed with  
 water to make the whole 1000 parts. A part of the  
 aqueous liquid composition was stored for 2 months at  
 5°C. Then, the composition was found to have a stable  
 solution state without precipitation of the reactive  
 15 dye.

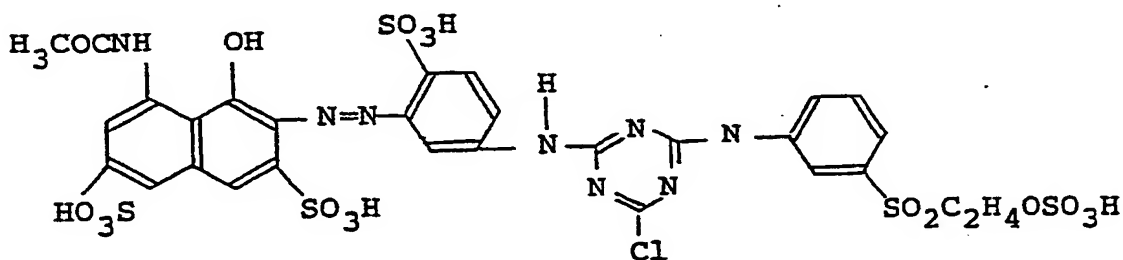


Example 7

20  $\epsilon$ -Caprolactam (20 parts) was mixed with a  
 reaction mixture (900 parts) which was a dye solution  
 obtained by a known method having 8% in a content of a  
 reactive dye represented by the formula (7) described

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1 below, 1% in a sodium chloride content and 2% in a  
sodium sulfate content. The mixture was formed into a  
clear solution, and sodium acetate (5 parts) was dis-  
solved therein. The resulting solution was adjusted to  
5 pH 5.5 using 10% sulfuric acid, and then mixed with  
water to make the whole 1000 parts. A part of the  
aqueous liquid composition was stored for 2 months at  
0°C. Then, the composition was found to have a stable  
solution state without precipitation of the reactive  
10 dye.



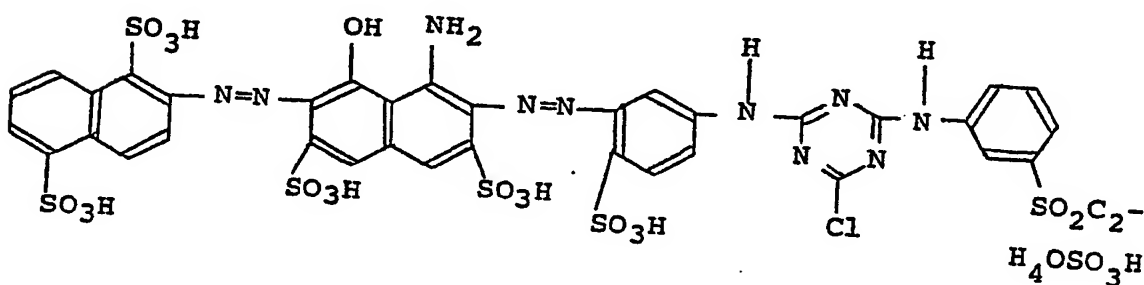
(7)

#### Example 8

A reactive dye of the formula (8) described  
below was produced by a known method, wherein the re-  
action mixture was subjected to salting-out, followed by  
15 filtration to obtain a wet cake, and a slurry-like mix-  
ture formed by mixing the wet cake with water was spray-  
dried. The powder obtained (180 parts) having 15% in a  
sodium chloride content and 3% in a sodium sulfate  
content was mixed with hot water (750 parts) of 50°C,  
20 and the mixture was stirred for 1 hour at 55°C to make a

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1 clear solution. Thereafter, the dye solution was al-  
 lowed to cool to ambient temperature, and ε-caprolactam  
 (20 parts) and sodium acetate (5 parts) were dissolved  
 therein in the order. The resulting solution was  
 5 adjusted to pH 5.3 using 10% sulfuric acid, and mixed  
 with water to make the whole 1000 parts. A part of the  
 aqueous liquid composition obtained was stored for 2  
 months at 0°C. Then, the composition was found to have  
 a stable solution state without precipitation of the  
 10 reactive dye.



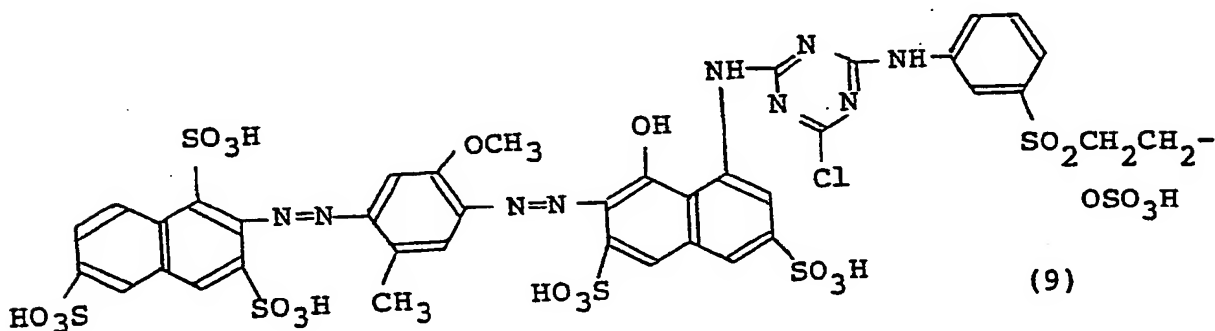
(8)

#### Example 9

A reactive dye of the formula (9) described  
 below was produced by a known method, wherein the re-  
 action mixture was subjected to salting-out, followed by  
 15 filtration to obtain a wet cake, and a slurry-like mix-  
 ture formed by mixing the wet cake with water was spray-  
 dried. The powder obtained (150 parts) having 18% in a  
 sodium chloride content and 4% in a sodium sulfate  
 content was mixed with hot water (800 parts) of 50°C,



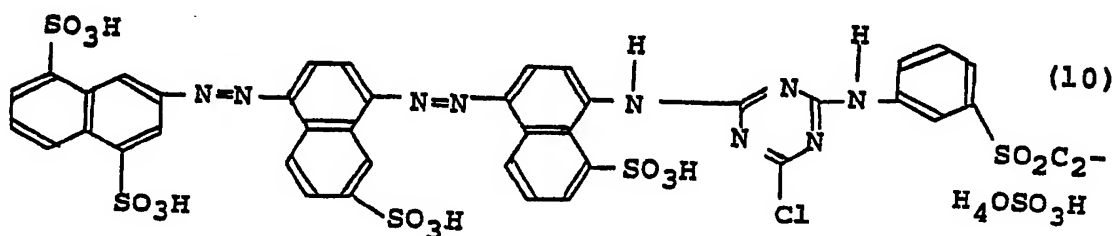
1 and the mixture was stirred for 1 hour at 55°C to make a  
clear solution. Thereafter, the dye solution was al-  
lowed to cool to ambient temperature, and ε-caprolactam  
(30 parts) and sodium acetate (5 parts) were dissolved  
5 therein in the order. The resulting solution was  
adjusted to pH 5.5 using 10% sulfuric acid, and mixed  
with water to make the whole 1000 parts. A part of the  
aqueous liquid composition obtained was stored for 2  
months at 5°C. Then, the composition was found to have  
10 a stable solution state without precipitation of the  
reactive dye.



#### Example 10

A reactive dye of the formula (10) described  
below was produced by a known method, wherein the  
15 reaction mixture was subjected to salting-out, followed  
by filtration to obtain a wet cake, and a slurry-like  
mixture formed by mixing the wet cake with water was  
spray-dried. The powder obtained (140 parts) having 13%  
in a sodium chloride content and 3% in a sodium sulfate  
20 content was mixed with hot water (800 parts) of 50°C,

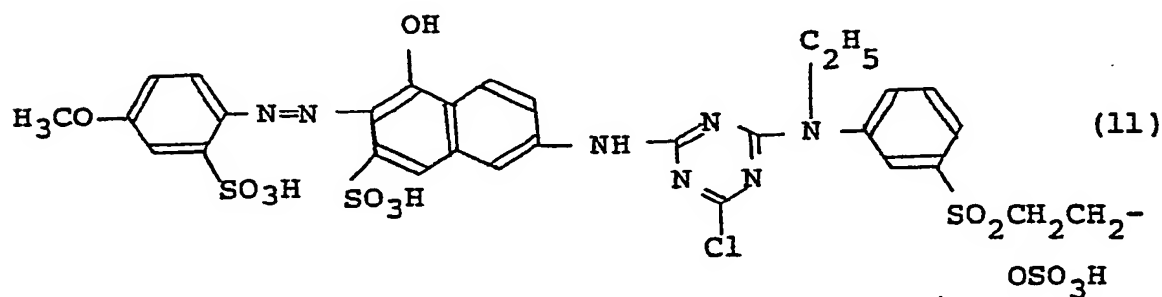
1 and the mixture was stirred for 1 hour at 55°C to make a  
clear solution. Thereafter, the dye solution was al-  
lowed to cool to ambient temperature, and ε-caprolactam  
(20 parts) and sodium acetate (5 parts) were dissolved  
5 therein in the order. The resulting solution was  
adjusted to pH 5.5 using 10% sulfuric acid, and mixed  
with water to make the whole 1000 parts. A part of the  
aqueous liquid composition obtained was stored for 2  
months at 5°C. Then, the composition was found to have  
10 a stable solution state without precipitation of the  
reactive dye.



#### Example 11

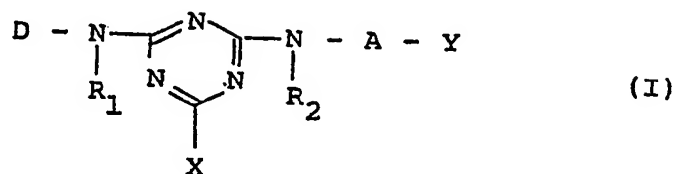
A reactive dye of the formula (11) described  
below was produced by a known method, wherein the  
15 reaction mixture was subjected to salting out, followed  
by filtration to obtain a wet cake, a slurry-like  
mixture formed by mixing the wet cake with water was  
spray-dried. The powder obtained (180 parts) having 18%  
in a sodium chloride content and 5% in a sodium sulfate  
20 content was mixed with hot water (750 parts) of 50°C,  
and the mixture was stirred for 1 hour at 55°C to make a

1 clear solution. Thereafter, the dye solution was al-  
 lowed to cool to ambient temperature, and ε-caprolactam  
 (30 parts) and sodium acetate (5 parts) were dissolved  
 therein in the order. The resulting solution was  
 5 adjusted to pH 5.3 using 10% sulfuric acid, and mixed  
 with water to make the whole 1000 parts. A part of the  
 aqueous liquid composition obtained was stored for 2  
 months at 0°C. Then, the composition was found to have  
 a stable solution state without precipitation of the  
 10 reactive dye.



WHAT IS CLAIMED IS:

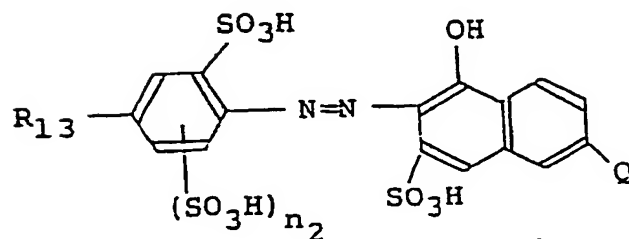
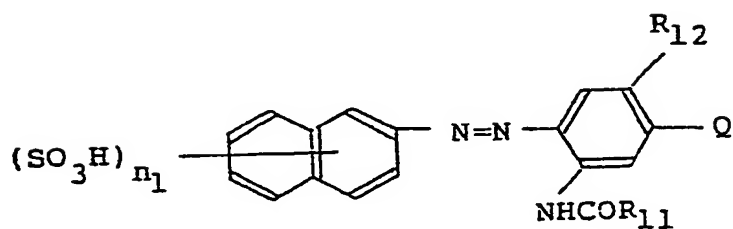
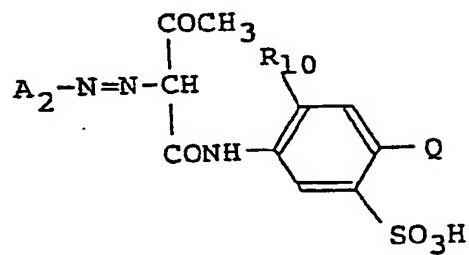
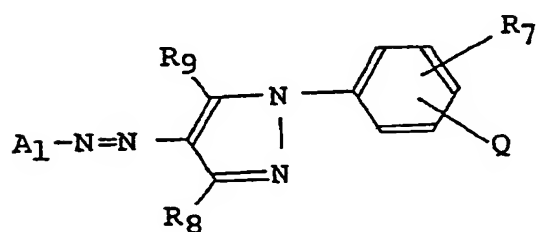
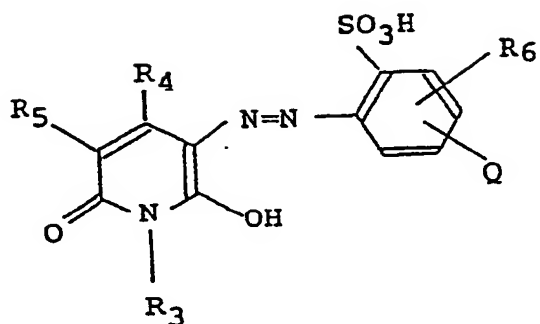
1. An aqueous liquid dye composition comprising 5 to 50% by weight of a reactive dye represented by the following formula (I)



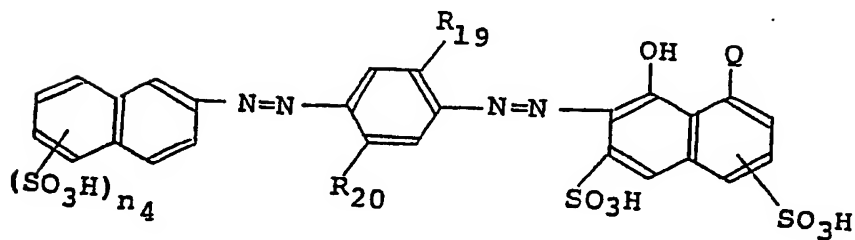
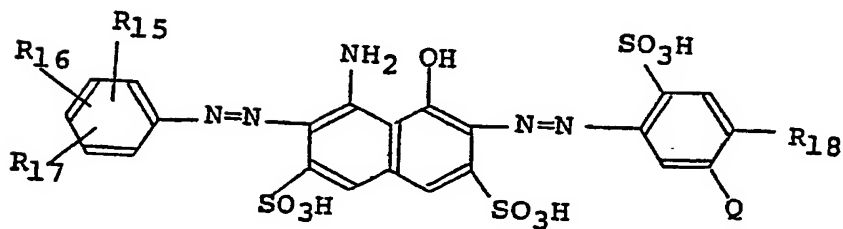
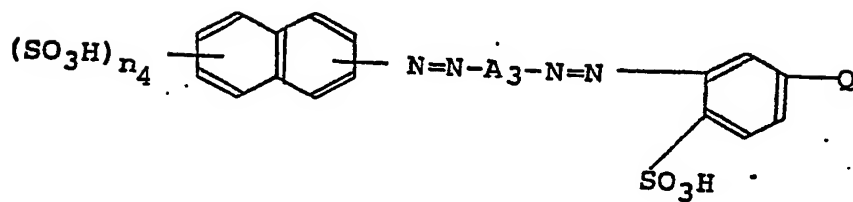
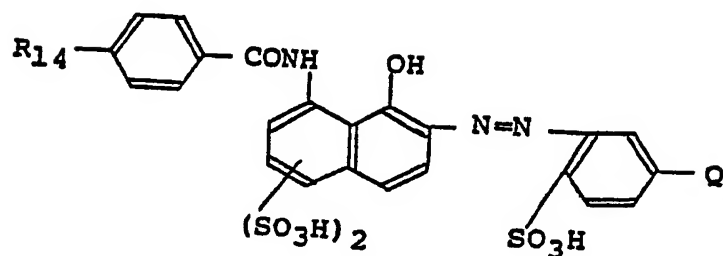
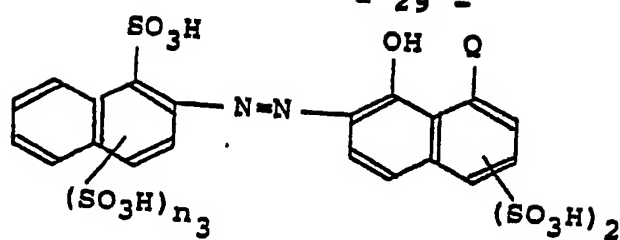
wherein D denotes a sulfo group-containing organic dye residue, R<sub>1</sub> and R<sub>2</sub> independently of one another denote a hydrogen atom or a C<sub>1</sub> to C<sub>4</sub> alkyl group unsubstituted or substituted with a halogen atom or a hydroxyl, cyano, C<sub>1</sub> to C<sub>4</sub> alkoxy, carboxy, carbamoyl, C<sub>1</sub> to C<sub>4</sub> alkoxy-carbonyl, C<sub>1</sub> to C<sub>4</sub> alkylcarbonyloxy, sulfo or sulfamoyl group, A denotes a phenylene group unsubstituted or substituted with one or two members selected from methyl, ethyl, methoxy, ethoxy, chlorine, bromine and sulfo, or a naphthylene group unsubstituted or substituted with one sulfo group, X denotes a halogen atom, and Y is a group of the formula -SO<sub>2</sub>CH=CH<sub>2</sub> or -SO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Z in which Z is a group which can be removed by the action of alkali, 0.1 to 10% by weight of ε-caprolactam and the balance of water, the composition having a pH value of 3 to 7.

2. The aqueous liquid dye composition according to Claim 1, wherein the reactive dye is at least one dye represented by the

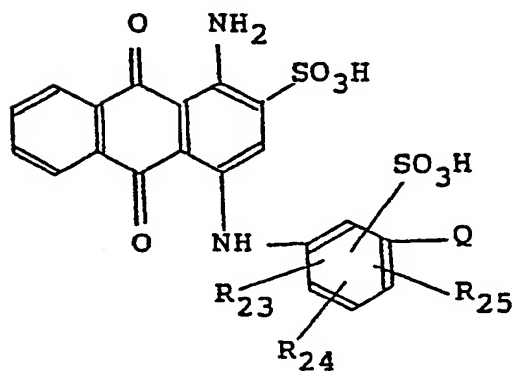
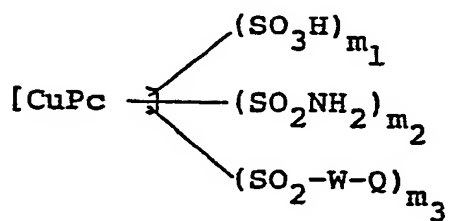
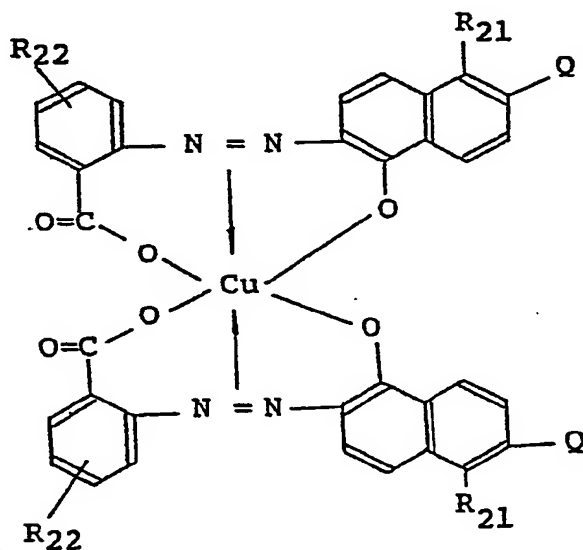
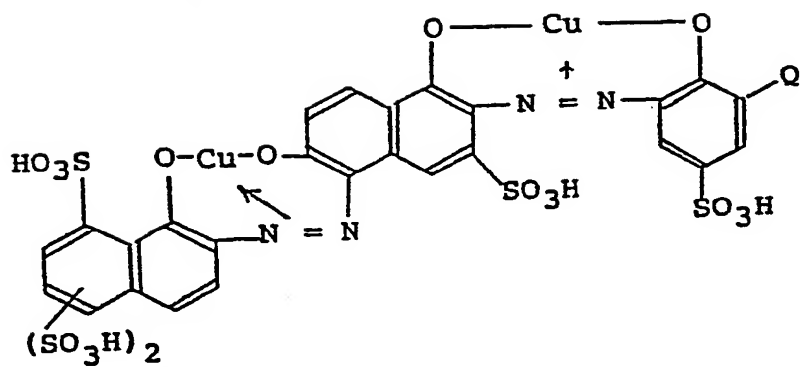
following formulae (all in free acid form),

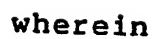


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R<sub>18</sub> is hydrogen or methyl,  
R<sub>19</sub> and R<sub>20</sub> are independently hydrogen, C<sub>1</sub>-C<sub>4</sub> alkyl  
or C<sub>1</sub>-C<sub>4</sub> alkoxy,  
R<sub>21</sub> is hydrogen or sulfo,  
R<sub>22</sub> is hydrogen, C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> alkoxy, sulfo  
or acetylamino,  
R<sub>23</sub>, R<sub>24</sub> and R<sub>25</sub> are independently C<sub>1</sub>-C<sub>4</sub> alkyl,  
A<sub>1</sub> and A<sub>6</sub> are independently unsubstituted or sub-  
stituted phenylene or naphthylene,  
A<sub>2</sub> is sulfophenyl substituted with methyl, ethyl,  
methoxy, ethoxy, phenoxy, acetylamino,  
propionylamino, HOOCCH<sub>2</sub>CH<sub>2</sub>CONH- or  
HOOCCH=CHCONH-, or naphthylene substituted  
with two or three sulfo groups,  
A<sub>3</sub> is a residue of naphthalenesulfonic acids,  
A<sub>4</sub> and A<sub>5</sub> are independently phenylene unsubstituted  
or substituted,  
W is aminoalkyl residue,  
m<sub>1</sub> is 1 or 2,  
m<sub>2</sub> is 0, 1 or 2,  
m<sub>3</sub> is 1 or 2, provided that m<sub>1</sub> + m<sub>2</sub> + m<sub>3</sub> ≤ 4,  
n<sub>1</sub> is 2 or 3,  
n<sub>2</sub> is 0 or 1,  
n<sub>3</sub> is 1 or 2,  
n<sub>4</sub> is 1, 2 or 3,  
and Q is -SO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Z in which Z is as defined in  
Claim 1.

3. The aqueous liquid dye composition according to Claim 1, wherein the composition comprises at least one of the buffers sodium or potassium acetate, sodium or potassium oxalate, sodium borate and sodium or potassium phosphates.

4. The aqueous liquid dye composition according to Claim 3, wherein the composition further comprises surfactants, dyeing auxiliary agents, hydrotropic agents, defoaming agents, antifreezing agents and/or antiseptics.

5. A method for preparing an aqueous liquid dye composition, which comprises dissolving in water a pre-determined amount of a reactive dye represented by the formula (I) according to claim 1, dissolving a pre-determined amount of  $\epsilon$ -caprolactam in the dye solution, adjusting the pH of the resulting solution within a range of 3 to 7, and adding water into the solution to make a dye content and an  $\epsilon$ -caprolactam content 5 to 50% by weight, and 0.1 to 10% by weight, respectively, based on the weight of the aqueous liquid dye composition.

6. A method for storing an aqueous liquid dye composition, which comprises preparing an aqueous liquid dye composition comprising 5 to 50% by weight of a reactive dye represented by the formula (I) according to claim 1, 0.1 to

10% by weight of  $\epsilon$ -caprolactam and the balance of water, the composition having a pH value of 3 to 7, and storing the composition in a closed vessel.

7. A method for dyeing fiber materials, which comprises using an aqueous liquid dye composition comprising 5 to 50% by weight of a reactive dye represented by the formula (I) according to claim 1, 0.1 to 10% by weight of  $\epsilon$ -caprolactam and the balance of water, the composition having a pH value of 3 to 7.





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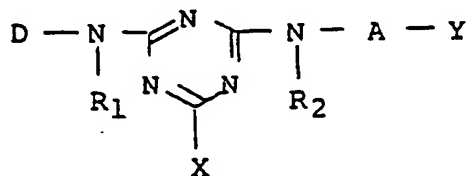
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⑤4 Reactive-dye-containing aqueous liquid composition.

⑥7 An aqueous liquid dye composition comprising 5 to 50% by weight of a reactive dye represented by the following formula,



wherein D denotes a sulfo group-containing organic dye residue, R<sub>1</sub> and R<sub>2</sub> independently of one another denote a hydrogen atom or a C<sub>1</sub> to C<sub>4</sub> alkyl group unsubstituted or substituted with a halogen atom or a hydroxyl, cyano, C<sub>1</sub> to C<sub>4</sub> alkoxy, carboxy, carbamoyl, C<sub>1</sub> to C<sub>4</sub> alkoxycarbonyl, C<sub>1</sub> to C<sub>4</sub> alkylcarbonyloxy, sulfo or sulfamoyl group, A denotes a phenylene group unsubstituted or substituted with one or two members selected from methyl, ethyl, methoxy, ethoxy, chlorine, bromine and sulfo, or a naphthylene group unsubstituted or substituted with one sulfo group, X denotes a halogen atom, and Y is a group of -SO<sub>2</sub>CH=CH<sub>2</sub> or -SO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Z in which Z is a splittable group by the action of an alkali, 0.1 to 10% by weight of ε-caprolactam and the balance of water, the composition having a pH value of 3 to 7, which can be stored for a long period of time at a low temperature such as 5°C or lower without deterioration in its solution state.

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**EP 0 234 573 A3**



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## EUROPEAN SEARCH REPORT

Application Number

EP 87 10 2710

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	DE-A-2 529 658 (HOECHST) * Page 4, lines 5-37; examples * ---	1-7	C 09 B 67/26 D 06 P 1/382 // C 09 B 62/02
Y	EP-A-0 127 456 (SUMITOMO) * Page 2, line 25 - page 3, line 17 * ---	1-7	
P,A	EP-A-0 208 829 (SUMITOMO) * Abstract * -----	1-7	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 09 B D 06 P
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 16-10-1990	Examiner DAUKSCH H.J.
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